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Thick Film Fabrication of Ferroelectric Phase Shifter Materials

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Various composites of BSTO combined with other non-electrically active oxide ceramics have been formulated. In general, the composites have adjustable electronic properties which can be tailored for use in phased array antennas and other phase shifting devices. The dielectric constant and the loss tangents have been reduced to enhance the overall impedance matching and thereby lowering the insertion loss of the device. In addition, the overall tunability, the change in the dielectric constant with applied voltage, is maintained at a sufficiently high level. The thickness limitation of the bulk materials is around 3-4 mils which can be used up to approximately 15 GHz. In order to increase the operating frequencies of the phase shifters, thick films were fabricated using non-aqueous tape-casting. The tapes were electrically characterized and compared to bulk ceramics. Also, laminated stacks with alternating layers of high dielectric constant and low dielectric constant were fabricated.

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1. INTRODUCTION

Phased array antennas can steer transmitted or received signals either linearly or in two dimensions without mechanically oscillating the antenna. These antennas are currently constructed using ferrite phase shifting elements. Due to the type of circuit requirements necessary to operate these antennas, they are costly, large and heavy. Therefore, the use of these antennas has been limited primarily to military applications which are strategically dependent on such capabilities. In order to make these devices available for many other commercial and military uses, the basic concept of the antenna must be improved. If ferroelectric materials could be used for the phase shifting element instead of ferrites, phased array antennas would be totally revolutionized.

A ceramic Barium Strontium Titanate, $Ba_{1-x}Sr_xTiO_3$, (BSTO), phase shifter using a planar microstrip construction has been demonstrated at 5-10 GHz.[1,2] BSTO/Oxide III (designated as oxide III as the materials are undergoing the patent filing process) composites have shown greatly improved electronic properties at both low (KHz-MHz) and microwave frequency regions (10 GHz).[3] Most notably loss tangents have been reduced to less than 0.002.[4] However, in order to meet the required performance specifications, at higher frequencies above 15 GHz, the thickness of the developed composites must be reduced to less than 4 mils. Therefore, thick films of these BSTO/Oxide III ceramics have been fabricated using non-aqueous tape-casting formulations. The electronic properties of the single layer tapes (less than 4 mils thick) will be compared to those of their bulk ceramic counterparts. Also a laminated stack of alternating high and low dielectric constant tapes has been fabricated and the electronic properties have been examined. SEM micrographs of the thick film electrode interfaces will also be presented.

2. EXPERIMENTAL

2.1 Ceramic Processing and Tape-Casting

Powder forms of Barium Titanate and Strontium Titanate were obtained from Ferro Corporation, Transelco Division, Pen Yan, N.Y. (product nos. 219-6 and 218 respectively), stoichiometrically mixed to achieve $Ba_{0.6}Sr_{0.4}TiO_3$ and ball-milled in ethanol using 3/16" alumina media for 24 hrs. The resulting BSTO was then air-dried, calcined at 1100^0C and mixed with the oxide (oxide III) in the proper weights (0, 10, 20, 40, 60 and 100 wt% Oxide III) and ball-milled again in a slurry of ethanol using the alumina grinding media for an additional 24 hrs. The resulting composites were then air-dried and subsequently sieved with a U.S. standard sieve series #60 (250 micron) sieve. The proper weight percent of the each ceramic composite was determined from the following equation and then added to the ceramic binder formulation, product # B73210, Ferro Corp. Electronic Materials Division, San Marcos, CA.

$$\text{Weight \% Ceramic} = 1 / [(0.01) + \{[1.0 / (18.5)(CSG)][\{100/(60-2(CSA-3))\} -1]\}] \tag{1}$$

where:

CSG = Ceramic Specific Gravity in g/cc
CSA = Ceramic Surface Area in m^2/g

The tapes were cast onto Teflon coated mylar sheets at a doctor blade setting of 20 mils. This resulted in green body thicknesses from 5 to 13 mils. The tapes were then removed from the mylar carriers. Single layer tapes were either fired at temperatures which had been previously determined by employing a deflectometer such as Mitutoyo digimatic indicator and miniprocessor (Mitutoyo Corp., Paramus N.J.) or were screen-printed with a conductive ink (see below) and then fired. The laminated structure was accomplished by stacking 5 layers of alternating high and low dielectric constant tapes. The part was uniaxially pressed in a heated plate (65^0C) to a pressure of 1000 psi. This structure was sintered at 1500^0C and subsequently metallized with ink #E3309 (see below). Metallization of the tapes was accomplished by screening a guard ring pattern on one side of the green (unfired) tape and a ground plane on the other side, as shown in Fig. 1. The ink used for this was product #E1162, 40%Au, 20%Pd and 40%Pt (firing temperature of 1350^0C), Ferro Corp., Electronic Materials Div., Santa Barbara, CA. Also fired tapes (10, 20, 40 and 60 wt% Oxide III) were screen printed with product #E3309 and subsequently fired at 850^0C.

Table 1 shows the densities which were obtained from He pycnometer measurements for the BSTO, BSTO/10wt% Oxide III, BSTO/20wt% Oxide III, BSTO/40wt% Oxide III, BSTO/60wt% Oxide III, Oxide III and the laminated tape stack.

2.2 Electronic Measurements

The dielectric constant, ε, is defined as

$$\varepsilon = \varepsilon' + i\varepsilon'' \tag{2}$$

where ε' is the real part and ε" is the imaginary part of the function. The loss, tan δ, is defined as:

$$\tan \delta = \varepsilon'' / \varepsilon' \tag{3}$$

and the % tunability of a material is determined using the following equation:

$$\% \text{ tunability} = \{ \varepsilon'(0) - \varepsilon'(\text{Vapp})\} / \{\varepsilon'(0)\} \tag{4}$$

The real part of the dielectric constant, ε', tan δ, and the % tunability were determined for all the composites. The electronic properties of the materials were measured using an HP4284A

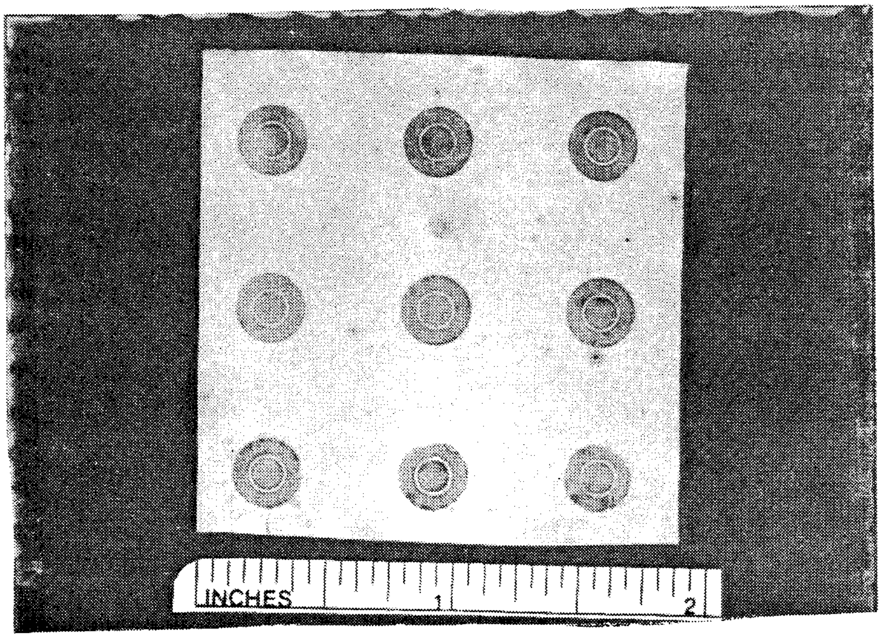

FIGURE 1. Photograph of sintered of front surface of BSTO/40 wt% Oxide III single layer tape (thickness = 2.55 mils, 65.4 microns) with co-fired ink (#E1162) guard ring electrodes.

TABLE I. Thicknesses and Densities of BSTO-Oxide III Ceramic Composite Tapes and Laminate.

Oxide III Content (wt%)	*Thickness (mils, microns)*	*Pycnometric Density (g/cc)*
0 wt%	4.4, 112.0	5.549
10 wt%	2.5, 64.3	5.413
20 wt%	3.6, 92.3	5.006
40 wt%	1.8, 45.4	4.420
60 wt%	2.7, 69.0	4.254
pure Oxide III	5.3, 133.7	3.584
Laminate	39.3, 991.0 7.8, 200.0	4.040

LCR meter at a frequency range of 1 KHz-1MHz. The dielectric constants were calculated using equation (5).

$$\varepsilon' = Ct/A\varepsilon_0 \qquad (5)$$

where:

ε' = dielectric constant of the layer, C = capacitance of BSTO

t = tape thickness, A = electrode area, and $\varepsilon_0 = 8.8542 \times 10^{-12}$ F/m

The tunability measurements were performed with an applied electric field of 2.0 V/micron (μm).

3. RESULTS AND DISCUSSION

3.1 SEM Micrographs

Fig. 2(a-c) shows SEM micrographs of a pure BSTO tape and BSTO/10 wt% Oxide III tapes. The BSTO/10 wt% Oxide III tape with the co-fired ink 1 = # E1162, recommended firing temp. = 1350^{0}C, is shown in Fig 2(b) and the BSTO/10 wt% Oxide III tape with the low fire ink 2 = # E3309 , recommended firing temp. = 850^{0}C, is shown in Fig. 2(c). Examination of the SEM of the tapes shows that ink 1 adheres well to the surface of these tapes since the sintering temperatures do not exceed the recommended firing temperature for the ink. As expected ink 2 also adheres well to these surfaces. SEM micrographs of the BSTO/20 wt% Oxide III and the BSTO/40 wt% Oxide III are shown in Fig. 3(a-d). Figs. 3(a) and 3(c) show the SEM micrographs of the BSTO/20 wt% Oxide III and the BSTO/40 wt% Oxide III tapes, respectively, with the co-fired ink, ink 1. Figs. 3(b) and 3(d) show tapes that have been electroded after sintering with ink 2. It is clear from these micrographs that the co-fired ink is peeling back from the tape surfaces, since the firing temperature is 1400^{0}C for tapes of these compositions. However, ink 2 is adhering well to the tape surfaces. Analysis of the grain size of the tapes shows that the grain size is slightly reduced as oxide III content is increased. No formation of secondary phases was evident. This was also the case for the bulk ceramic materials.[3]

3.2 Electronic Properties

The results for the electronic properties of the BSTO/Oxide III bulk ceramics, tapes and laminated stack are shown in Table II. The dielectric constants and loss tangents of the tape-cast specimens, similar to the bulk composites, decrease with increase in oxide III content and vary less than 2% with frequency (from 1KHz-1MHz). The magnitude of the dielectric constants are very similar to those of the bulk ceramics, except for the 20 wt% and 40 wt% tapes with the co-fired electrodes (#E1162). As shown in Fig. 4, the dielectric constants of these tapes are less than those of the corresponding bulk ceramic composite samples. This may be due to the delamination of the electroding material as shown in Figs. 3(a) and 3(c). As shown in Fig. 5, the loss tangents of the tapes are also similar to those measured for the bulk ceramics. The percent tunability of the tapes as well as the bulk material is around 15% with 2.00 V/μm at 10 wt% oxide III and only reduces to around 12% at 60 wt% oxide III. This trend was explained previously in the bulk ceramics[4] by the position of the Curie temperatures and the size of the additive (oxide III). The addition of oxide III shifts the Curie temperature of the material to -30^{0}C (from 1 wt% to 50 wt% oxide content) and to <-55^{0}C for >60 wt% oxide content.[4] This accounts for the reduction in the loss tangent. The small size of the additive permits this tunability to be maintained up to 60 wt% oxide III content.

4. CONCLUSIONS

Non-aqueous tapes of BSTO/Oxide III ceramics have been fabricated and characterized. All the tapes have demonstrated adjustable electronic properties which are similar in value to those obtained for the bulk ceramics. The BSTO/Oxide III tapes and bulk materials exhibit low loss

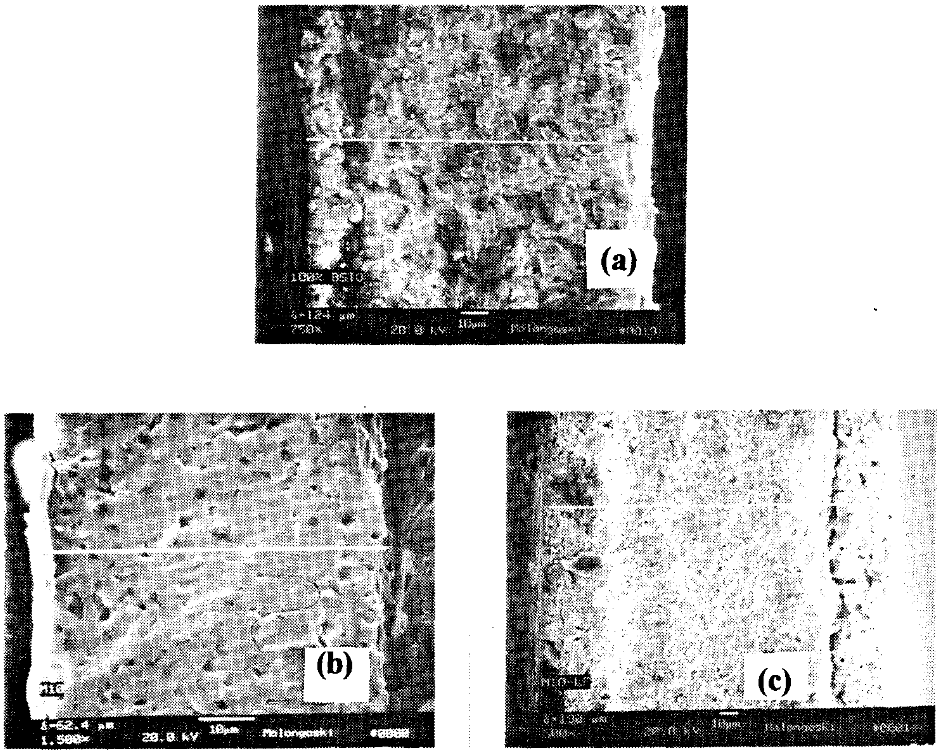

FIGURE 2. SEM micrographs of (a) a BSTO tape electroded with co-fired ink (#E1162), (b) BSTO/10 wt% Oxide III tape electroded with co-fired ink (#E1162), (c) BSTO/10 wt% Oxide III taped electroded with ink (#E3309).

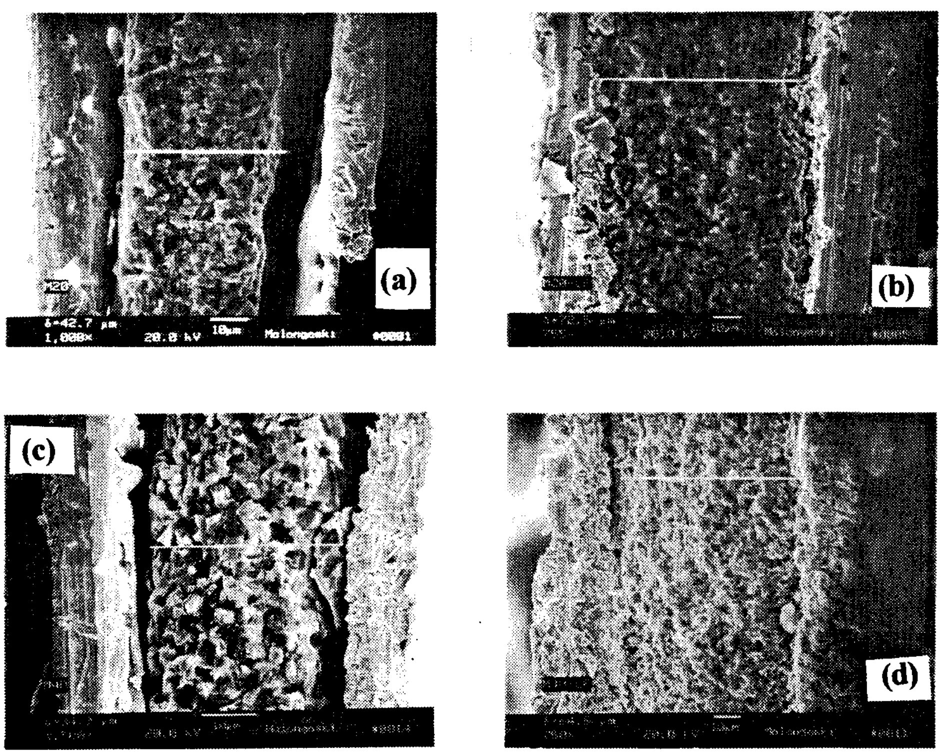

FIGURE 3. SEM micrographs of (a) BSTO/20 wt% Oxide III tape electroded with co-fired ink (#E1162), (b) BSTO/20 wt% Oxide III tape electroded with ink (#E3309), (c) BSTO/40 wt% Oxide III tape electroded with co-fired ink (#E1162), (d) BSTO/40 wt% Oxide III tape electroded with ink (#E3309).

TABLE II. Electronic Properties of BSTO (Ba = .60) and Oxide III Composite Bulk Ceramics, Tapes, and Laminated Tape Stack measured at 1 KHz.

BULK CERAMICS

Oxide III Content (wt %)	*Dielectric Constant*	*Loss Tangent*	*% Tunability*	*Electric Field (V/μm)*
0.0	3299.08	0.0195	19.91	0.73
10.0	1414.70	0.0013	10.27	2.00
20.0	1079.21	0.0009	15.95	2.33
40.0	416.40	0.0009	19.81	2.5
60.0	117.67	0.0006	11.08	2.70
100.0	13.96	0.0009		

TAPES (Ink 1 = #E1162, 1350^{0}C, Ink 2 = #E3350, 850^{0}C).

0.0	3192.20	0.0056	43.52	2.00
10.0 (ink 1)	1390.20	0.0015	15.03	2.00
10.0 (ink 2)	1245.10	0.0024	11.40	2.00
20.0 (ink 1)	616.44	0.0012	15.45	2.00
20.0 (ink 2)	779.10	0.0049	14.30	2.00
40.0 (ink 1)	193.60	0.0012	16.50	2.10
40.0 (ink 2)	357.30	0.0041	14.00	2.00
60.0 (ink 1)	91.16	0.0008	10.41	2.00
60.0 (ink 2)	65.67	0.0183	11.70	2.00
100.0	2.81*	0.0621*		
LAMINATE	21.34	0.0086	14.48	2.00

* Not fully sintered

** Tunability was measured perpendicular to laminate direction due to design considerations for antennas.

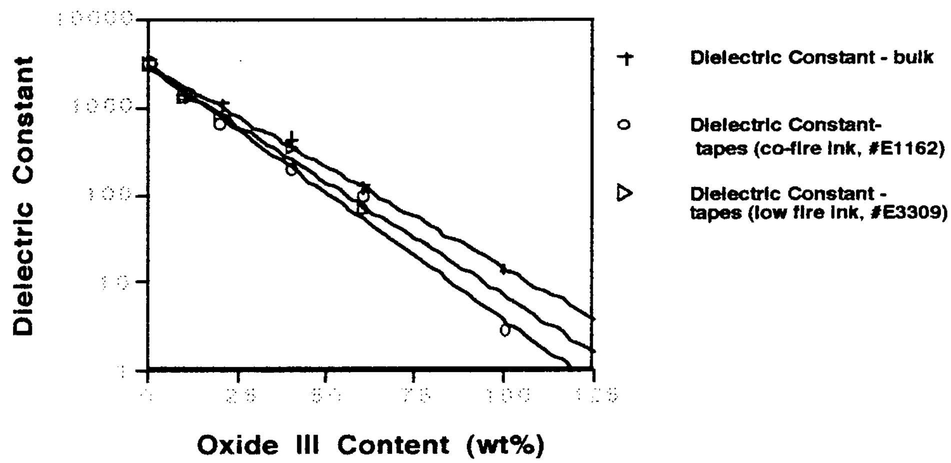

FIGURE 4. Semi-log Plot of Dielectric Constant versus Oxide III Content of the Bulk Ceramics and the Tapes Measured at 1 KHz (lines represent best fit to the data).

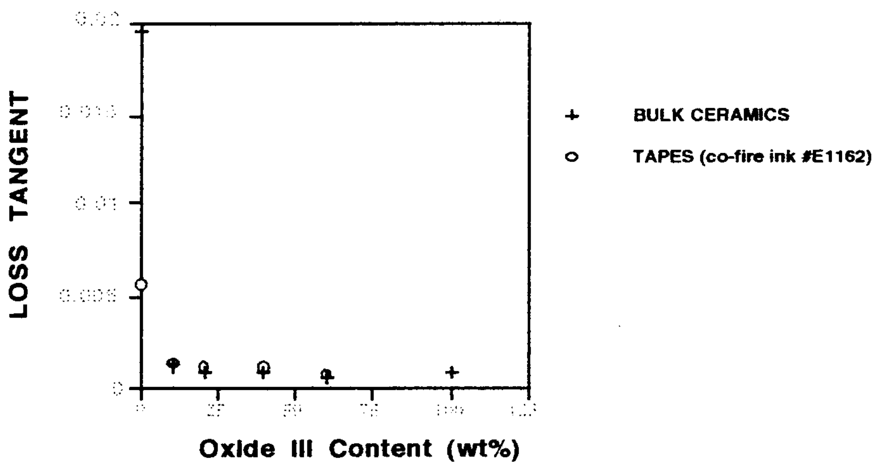

FIGURE 5. Loss Tangent versus Oxide III Content (wt%) of the Bulk Ceramics and the Tapes measured at 1 KHz.

(<0.005) and tunability of 12-15% (2.0 V/µm) up to 60 wt% oxide III content. The laminated tape stack displayed a very low dielectric constant (~22.0) and a high tunability (14.5 %). Incorporation of the single layer tapes and the laminated stacks into co-planar waveguide phase shifters, in collaboration with ARL-EPSD and NRL, is currently in progress.

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